

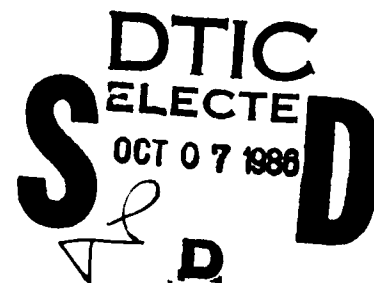
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Synthesis, Characterization, and Charge Distribution of
Bis(4-t-butylpyridine)bis(3,5-di-t-butylquinone)ruthenium

By

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**Synthesis, Characterization, and Charge Distribution of
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Abstract

The synthesis and characterization of bis(4-*t*-butylpyridine)bis(3,5-di-*t*-butylquinone)ruthenium is reported. A crystallographic molecular structure determination carried out on the complex has shown that it exists as the trans isomer and that ligand C-O lengths are relatively long for a semiquinone complex being at the bottom end of the range observed for catecholato complexes. Both quinone ligands appear structurally and electronically equivalent. The complex is diamagnetic and shows a well-resolved NMR spectrum. Electrochemically, the complex undergoes four redox processes, all of which most likely involve both metal and quinone ligands. There are charge-transfer bands in the visible region, and an exceptionally intense and structured band in the near infrared region. The ground state is viewed as a mixture of bis(4-*t*-butylpyridine)bis(3,5-di-*t*-butylsemiquinone)ruthenium(II) and bis(4-*t*-butylpyridine)bis(3,5-di-*t*-butylcatecholato)ruthenium(IV), with the former dominant.

Metal-ligand electron transfer occurs as a fundamental step in redox processes of complexed metal ions, but only in rare cases has it been studied directly. Intramolecular charge separation induced photochemically contributes to the activity of photocatalysts where oxidative and reductive centers result from transfer of charge between localized metal and ligand electronic levels. Ruthenium bipyridine and diimine complexes have been of particular interest in this context⁵ and recent studies on o-quinone complexes indicate even more facile electron transfer properties.⁶ Quinone ligands⁷ chelated to metal ions as either semiquinone or catecholate, form complexes with quinone π^* electronic levels and metal d-orbitals close in energy yet discrete in the molecular orbital structure of the complex.⁸ This has permitted studies on parameters which direct charge distribution within the metal-quinone chelate ring.⁹

Air oxidation of $\text{Ru}(\text{bpy})_2(\text{DBCat})$ yields the $\text{Ru}^{2+}(\text{bpy})_2(\text{DBSq})^+$ cation with oxidation occurring at the catecholate ligand.¹⁰ This charge distribution has been determined from the structural features of the cation¹¹ and from electronic spectroscopic considerations.¹⁰ Complexes containing two quinone ligands bonded to ruthenium were prepared by treating $\text{Ru}_2(\text{OAc})_4\text{Cl}$ with DBCat. Addition of excess 4-t-butylpyridine gave $\text{Ru}(\text{t-Bupy})_2(\text{DBQ})_2$.¹² The results of a crystallographic molecular structure determination on the complex show that the quinone ligands are bonded strongly to the metal in the trans structure of the molecule (Figure 1).¹³ Ruthenium-oxygen bond lengths in this structure are 0.05Å shorter than values found¹¹ for $\text{Ru}(\text{bpy})_2(\text{DBSq})^+$ but are 0.02Å longer than the 1.974(4)Å length

reported for trans-dichlorobis(triazene-1-oxidato)ruthenium(IV).¹⁴ Quinone C-O lengths of the structure are intermediate between values expected for a semiquinone ligand, 1.29Å, and a catecholate, 1.34Å. The equivalence of the two quinone ligands, and the absence of anisotropy in the oxygen thermal ellipsoids provides evidence that the two quinone ligands are of the same charge, i.e. (DBCat)₂ or (DBSq)₂, and not of mixed charge, (DBCat)(DBSq). Moreover, such mixed valence systems commonly show very broad, relatively weak, near infrared absorption,^{6a,15} not evident here. Ru(t-bupy)₂(DBQ)₂ is diamagnetic and has a proton nmr spectrum consistent with the trans structure.¹⁶ Cyclic voltammetry, in 1,2-dichloroethane (100 mV/s), shows four couples at +0.62, -0.19, -1.12 and -2.00 (vs Fc⁺/Fc), the most negative being irreversible. Assignments will be discussed elsewhere.¹²

The optical absorption spectrum consists of bands at 280 nm (13,000 M⁻¹cm⁻¹), 325 (4060), 400 (3780), and 580 (1100) in the UV and visible regions. The most interesting feature is a remarkably intense, structured, band centered at 1160 nm (35,300) in the near-IR (Figure 2). It is surely significant that the species Ru^{II}(bpy)₂(DBSq)⁺ and Ru^{II}py₄(DBSq)⁺ show similar, structured, intense bands at comparable energies¹⁰ and assigned as Ru(II)→DBSq metal to ligand charge transfer (MLCT) transitions.¹⁷

The photoelectron spectrum¹⁸ shows a ruthenium 3d_{3/2} signal at a bonding energy of 280.8 eV, being the same as that found for [Ru^{II}(bpy)₂(DBSq)]PF₆.¹⁰

There are two limiting electronic structures for the title species, Ru^{II}(t-bupy)₂(DBSq)₂ and Ru^{IV}(t-bupy)₂(DBCat)₂. We favor

the ruthenium(II) formulation as the dominant (but not exclusive) contribution to the structure for the following reasons: a) the near-IR absorption appears to be a MLCT feature, and its presence therefore favors Ru(II); b) the PES bonding energy is appropriate for Ru(II), rather than Ru(III) (ca 281.5-282 eV)^{19a} or Ru(IV) (ca 282 eV).^{19b,20}

In its Ru(II) form, this would be the first structurally characterized example of a complex in which two equivalent semi-quinone ligands lie in the same plane. The diamagnetism observed in this case must result from strong ligand-ligand coupling through the ruthenium center.

The species $\text{Ru}^{2+}(\text{bpy})_2(\text{DBSq})^+$ has a structure^{10,11} distorted towards the electronic isomer $\text{Ru}^{2+}(\text{bpy})_2(\text{DBCat})^+$. We have previously proposed¹⁰ that the existence of the low-lying, near infrared MLCT state is responsible, through mixing into the ground state, for this distortion. The relatively long C-O bonds observed in the title compound probably reflect similar mixing and indicate that the complex has Ru(IV) character. Note that the analogous complex $\text{Mn}^{2+}(\text{py})_2(\text{DBCat})_2$ has C-O bond lengths (1.35Å) significantly longer than observed here, but that this manganese(IV) complex electronically isomerized to $\text{Mn}^{2+}(\text{py})_2(\text{DBSq})_2$ when cooled below about 250 K.^{6b} The title ruthenium(II) complex does not show similar temperature dependence.

In summary, the title compound, as a consequence of intramolecular electron transfer, shows properties of being both a Ru(II) and a Ru(IV) species, but with the former dominant.

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Supplementary Material Available. Tables of atomic positional and thermal parameters and observed and calculated structure factors for bis(4-t-butylpyridine)bis(3,5-di-t-butylquinone)ruthenium (18 pages). Ordering information is given on any current masthead page.

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13. Triclinic, P1, $a = 9.072(2)\text{\AA}$, $b = 11.068(2)\text{\AA}$, $c = 11.554(2)\text{\AA}$,
 $\alpha = 90.25(2)^\circ$, $\beta = 99.51(2)^\circ$, $\gamma = 95.96(2)^\circ$,
 $V = 1137.7(3)\text{\AA}^3$ at 297°K, $D_{\text{calc}} = 1.185\text{ gcm}^{-3}$,
 $D_{\text{expt}} = 1.17(2)\text{ gcm}^{-3}$, $Z = 1$, $R = 0.048$, $R_w = 0.059$
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16. ^1H NMR (CDCl_3) δ 1.03(s, 18H), 1.42(s, 18H), 1.64(s, 18H), 5.85(d, 2H, $^4J = 5\text{ Hz}$), 6.43(2d, 4H, $^3J = 13$ and $^5J = 3\text{ Hz}$), 7.07(2d, 4H, $^3J = 13$ and $^5J = 3\text{ Hz}$), and 7.73(d, 2H, $^4J = 5\text{ Hz}$).

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20. A bis(catecholato)ruthenium(IV) electronic isomer might have a binding energy depressed by the electron donating catechol from the Ru(IV) into the Ru(II) binding energy region.

Based on previous experience²¹ it is very unlikely that such a dramatic shift would be observed; however, the possibility is being investigated.

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Figure 1. ORTEP plot of the centrosymmetric $\text{Ru}(\text{t-Bupy})_2(\text{DBQ})_2$ molecule. Standard deviations on Ru-O and Ru-N bond lengths are 0.003 Å and 0.005 Å on C-O lengths.

Figure 2. Near infrared spectrum of $\text{Ru}(\text{t-Bupy})_2(\text{DBQ})_2$ showing absorptions in the 1100 nm region and disappearance of these absorptions upon coulometric oxidation of the complex.

